Location of caoutchouc in teak

Koichi Yamamoto* and Maruli H. Simatupang**

*Japan International Research Center for Agricultural Sciences, Forestry Division, 1-2 Owashi, Tsukuba, Ibaraki, 305 Japan
**University Sains Malaysia, Unit of Wood, Paper and Coating Technology, School of Industrial Technology, 11800 Penang, Malaysia

Summary

Thin sections of teak heartwood were extracted with acetone or acetone and chloroform successively and analyzed by X-ray photoelectron spectroscopy(XPS). The latter extraction decreased the content of C1 (carbon bonded to carbon and/or hydrogen) and increased that of C2 (carbon bonded to one oxygen) in XPS C1s spectra, although the former extraction did not change the XPS spectra clearly, compared with unextracted sections. The water repellency of the wood surface significantly reduced during successive extraction with acetone and chloroform. Caoutchouc extracted with chloroform is responsible for the water repellency of teak wood. Localization of caoutchouc in the cells of teak was investigated using scanning electron microscopy. Caoutchouc seemed to exist not only in parenchyma cells but also in fibers and vessels.

Keywords; *Tectona grandis*, teak, heartwood, parenchyma cell, caoutchouc, water repellency, contact angle, x-ray photoelectron spectroscopy.

Introduction

Teak is one of the most valuable wood species in the world, and is currently cultivated in many parts of the world (Premrasmi and Dietrichs 1967, Dahms 1989). The wood has outstanding properties in durability (Da Costa *et al.* 1958, Sandermann and Simatupang 1966, Findlay 1985), iron stains (Ser and Neo 1982), and dimensional stability (Choong and Achmadi 1991). The good dimensional stability as well as the good abrasion resistance are ascribed to the caoutchouc which is reported occurring in parenchyma of heartwood (Sandermann and Simatupng 1966). The hydrophobic properties and the good abrasion resistance, however, can not be wholly explained by the occurrence in parenchyma cells.

The focus of this paper is to elucidate not only the effect of caoutchouc on the surface characteristics of teak wood using X-ray photoelectron spectroscopy (XPS), but also the localization of caoutchouc in cells using scanning electron microscopy. XPS is one of the most effective and sensitive tools for the surface analysis of solid wood.

Materials and Methods

Teak (*Tectona grandis* L. f.) wood sample used in this experiment was obtained from Cepu, Central Java, Indonesia. The heartwood of the sample was air-dried to about 10-11 % moisture content. Radial sections of 60 um in thickness and 10x10 mm in area were serially microtomed using a new disposable microtome blade, cleaned with acetone to remove oil (Ruddick *et al.* 1993). Two third of the sections were soaked with acetone and allowed to stand for 4 days changing the solvent once a day. The half of the acetone extracted sections were then soaked with chloroform and allowed to stand for 4 days changing the solvent once a day. Unextracted, acetone-extracted, and acetone and chloroform-extracted sections were subjected to the examination by x-ray photoelectron spectroscopy, scanning electron microscopy, and determination of contact angle.

XPS analysis were performed within several days after the extraction of the sections. Until the XPS analysis, all the sections were stored in dark clean glassware at room temperature to minimize surface contamination. The spectra were measured in a Shimadzu ESCA 850 electron spectrometer. The spectrophotometer operating pressure was 0.5 - 1.0 x 10^{-5} Pa. The unmonochromatized MgKa excitation source was operated at 8 kV and 30 mA. The emitted photoelectrons were collected from a circular area, 5 mm in diameter. High-resolution narrow-scan spectra for quantitative analysis were

Presented at 3rd Conference on Forestry and Forest Products Research 1995 (CFFPR-95), 3-4 October 1995, Kuala Lumpur

measured for the C1s and O1s core levels at a 75 eV pass energy. Peak areas, determined after background subtraction, were used to measure relative element concentrations.

Location of caoutchouc was examined with a JEOL JSM-840A scanning electron microscope. Microtomed section surfaces were coated with gold. Observation was done at 5 kV and 3 x 10^{-11} A.

To evaluate the water repellency, the contact angle was measured. Droplets of 10 ul distilled water at 25 C were placed on the center of each section. The contact angle was measured 5,.20, 40, and 600 second after application on macrophotographs taken with a camera. Three sections were used in each test and mean value was calculated.

Results and Discussions

X-ray photoelectron spectroscopy

The surface of unextracted heartwood section showed the XPS C1s spectrum which is rich in C1 component (Fig. 1a). Carbon atoms in woody materials have been classified into four categories which correspond to C1: -CHx, C2: hydroxyl or ether, C3: carbonyl or acetal, and C4: carboxyl or ester (Dorris and Gray 1978). The spectrum is similar to those of untreated surfaces of *Liriodendron tulipifera* sapwood (Hon 1984), *Cryptomeria japonica* sapwood (Kiguchi 1990), *Pinus sylvestris* sapwood (Nussbaum 1993). Extractives possibly migrated onto the surface of sections during sample preparation such as microtoming, are exhibiting a strong C1 peak of the XPS C1s spectra (Hon 1984, Yamamoto and Ruddick 1993).

Extraction with acetone did not change its shape of the C1s spectra clearly, although a slight decrease of C2 component was recognized (Fig. 1b). The O/C ratio of the surface of the section determined by XPS decreased with acetone extraction (Table 1). The decrease of the O/C ratio suggested that caoutchouc with hydrophobic nature appeared on the surface of the section during the acetone extraction. Caoutchouc is a main hydrocarbon in Teak wood (Sandermann et al. 1963) .

XPS C1s spectrum of chloroform extracted section pre-extracted with acetone showed a decrease of the C1 component and an increase of the C2 component (Fig. 1c). This would be explained by the decrease of caoutchouc from the surface of the section with the chloroform extraction. The increase of O/C ratio also supported the decrease of caoutchouc. Probably, the caoutchouc was not removed completely, because the O/C ratio is 0.40 which is still low value. The O/C ratio of a solid residue of supercritical extraction of *Populus tremuloides* is 0.65 (Ahmed *et al.* 1988), that of extracted chips of Pinus silvestris is 0.42 (Mjoberg 1981), and that of extractive-free sections of Ponderosa pine and Douglas-fir is 0.585 and 0.661 respectively (Ruddick *et al.* 1993). The low O/C ratio of the surface of teak cell walls suggests the occurrence of compounds poor in oxygen. It was postulated that some tropical wood with high Klason lignin content contain condensed phenolics, which apparently canbe extracted with sodium hydroxide solution. According to Reyes (1938) and Timell (1958), Teak has a Klason lignin content of 35 % and 31 % respectively (cited according to Rowell 1984).

Table 1. O/C ratio of unextracted section, extracted section with acetone, and extracted section with acetone and chloroform successively

Specimen	O/C
Unextracted section	0.24
Extracted section with acetone	0.16
Succesive extracted section with acetone and chloroform	0.40

Scanning electron microscopy

The scanning electron microscopic observations of the unextracted sections reveal that lumens of all cell types are more or less covered with extraneous materials. However, the amounts of such materials are much abundant in parenchyma cells than in fibers and vessel elements (Fig. 2a and 2b). Not only the lumens but also the cut surface of parenchyma cell walls are usually covered with thick extraneous materials (Fig. 2a). On the contrary, the cut surface of fibers are relatively clear and free of

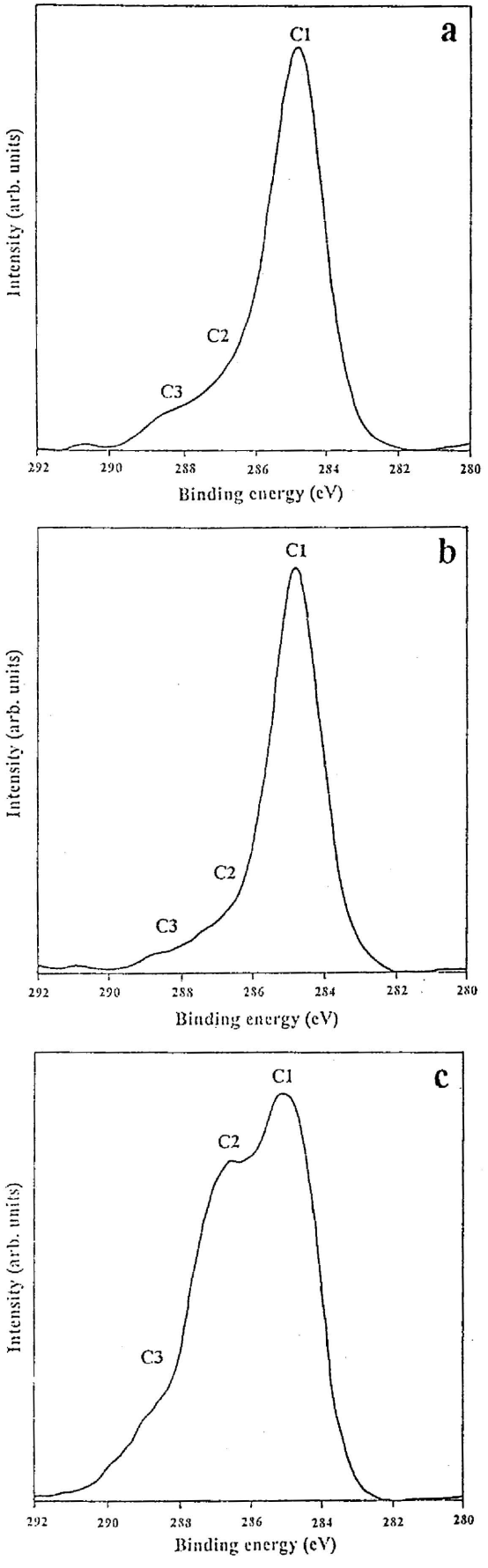

Fig. 1. XPS C1s spectra of teak heartwood; a unextracted section, b extracted section with acetone, c extracted section with acetone and chloroform successively.

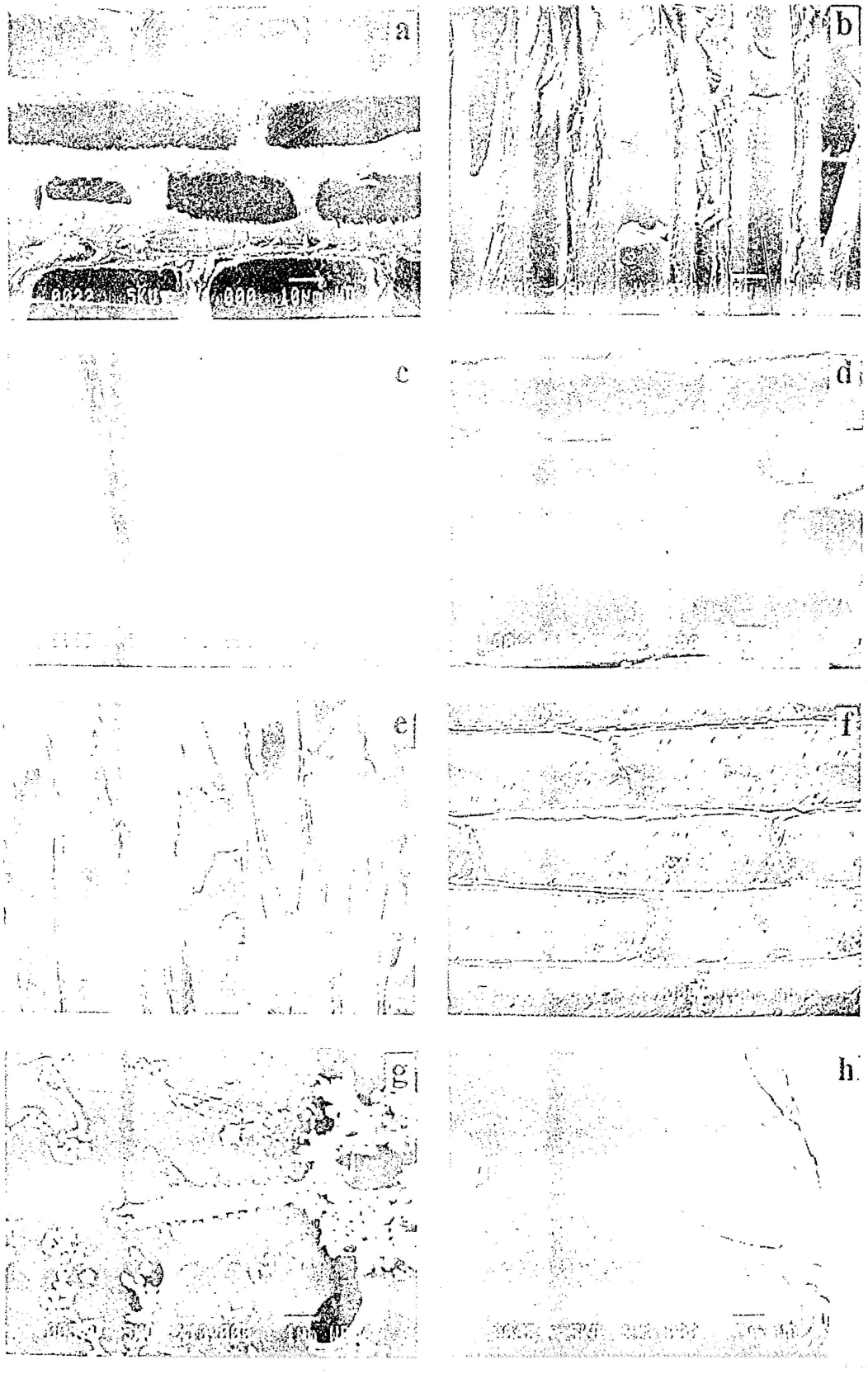

Fig. 2. Transverse surfaces of teak heartwood; a, b, c; unextracted, d, e; extracted with acetone, f, g, h; extracted with acetone and chloroform successively. a) ray parenchyma cells, b) fibers, c) lumen of fiber, d) ray parenchyma cells, e) fibers, f) ray parenchyma cells, g) lumen of ray parenchyma cell, h) lumen of fiber.

such extranious compounds (Fig. 2b). This phenomenon suggests that parenchyma cell walls contain extractives which are absent in fibers and vesell elements. These compounds may diffuse to the surface of the cuttings and form a layer. The fiber cell lumens are sometimes covered with extraneous materials covering the microfibril (Fig. 2c).

Extraction with acetone does not change the feature of surface morphology clearly (Fig. 2d and 2e). Most of the extraneous materials seems to remain on the surface of the specimens, even after acetone treatment. This observation was correspond with the results of XPS.

Successive extraction with acetone and chloroform removes most of extraneous materials (Fig. 2f and 2g). The lumen surfaces of parenchyma cells become smooth and clear, remaining deposits may be originated from the residue of cytoplasmic organelles (Fig. 2g). The lumen of fiber cells is relatively clear showing a microfibril orientation (Fig. 2h), which is not feasible in untreated section (Fig. 2c) . The materials extracted with chloroform could be caoutchouc (Sandermann and Dietrichs 1959). Caoutchouc seemed to be not only located in parenchyma cells but also in fibers and vessel elements. However, it has been considered caoutchouc to be present only in parenchyma cells and tended to be restricted to the heartwood (Sandermann *et al.* 1963). Further studies about the localization of caoutchouc is required.

Water repellency

The result of contact angle measurements is shown in Table 2. Water repellency of unextracted section was relatively higher than that of the other wood species described in literature (Yamamoto and Inoue 1990, Nussbaum 1993) .

Table 2. Contact angle of unextracted section, extracted section with acetone, and extracted section with acetone and chloroform successively

Specimen	Time	Contact angle
Unextracted section	5	93
	20	89
	40	89
	600	79
Extracted section with acetone	5	97
	20	96
	40	93
	600	83
Successive extacted section with acetone and chloroform	5	85
	20	81
	40	72
	600	60

The extraction with acetone increased their contact angle slightly (Table 2). This would suggest acetone extraction removed most of extractives other than polyisoprenoid such as caoutchouc, and the caoutchouc appeared on the surface of the section. Caoutchouc is not soluble in acetone. The caoutchouc could increase water repellency slightly.

Chloroform extraction after acetone extraction resulted in a considerable decrease of contact angle. The caoutchouc redistributed on the surface of section could be removed mostly with the chloroform extraction. Caoutchouc is soluble in chloroform (Sandermann and Dietrichs 1959). The caoutchouc is considered to be responsible for the resistance of teak to chemical attacks and perhaps for the low rate of shrinkage too (Narayanamurti and Singh 1960).

The contribution of caoutchouc to the natural durability of the heartwood is not yet clarified. The coexistence of active and inactive compounds with hydrophobic properties, e.g. caoutchouc, may give the teakwood its high natural durability. Caoutchouc, a polymer with unsaturated bonds, is durable for 2000 years in teakwood. Pure caoutchouc alone is very sensitive against oxydation. A newly isolated antioxydant from teakwood may protect the sensitive caoutchouc in teakwood (Simatupang and

Rosamah 1994). It is postulated that durable wood species contain active as well as inactive compounds with hydrophobic properties together with antioxydants to protect the latter.

Conclusions

Caoutchouc has an important role on the water repellency of teak. Chloroform extraction decreased the amount of C1 components and increased those of C2 components of the surface of teakwood, as shown by XPS C1s spectra. It seems that the used successive extraction with acetone and chloroform do not remove all extractives, because the O/C ratio of the treated specimens is still relatively low. SEM observations suggest that caoutchouc is not only found in parenchyma cells but also in fibers and vessels. The occurrence of caoutchouc in cell walls of parenchyma is also suggested. Future work on the study of brominated wood using x-ray microprobe analyzer should give more details of the localization of caoutchouc.

References

Ahmed, A., Adnot, A., and Kaliaguine, S. 1988. ESCA analysis of partially converted lignocellulosic materials. J. Appl. Polym. Sci. 35, 1909-1919.

Choong, E. T. and Achmadi, S. S. 1991. Effect of extractives on moisture sorption and shrinkage in tropical woods. Wood Fib. Sci. 23, 185-196.

Da Costa, E. W. B., Rudman, P., and Gay, F. J. 1958. Investigations on the durability of *Tectona grandis*. Emp. For. Rev. 37, 291-298.

Dahms, K. -G. 1989. Das Holzportrait Teak. Holz als Roh- und Werkstoff 47, 81-85.

Dorris, G. M. and Gray, D. G. 1978. The surface analysis of paper and wood fibers by ESCA (Electron spectroscopy for chemical analysis). I. Application to cellulose and lignin. Cellul. Chem. Technol. 12, 9-23.

Findlay, W. P. K. 1985. Preservation of timber in the tropics. Martinus Nijhoff/Dr. W.Junk Publishers, Dordrecht.

Hon, D. N. -S. 1984. ESCA study of oxidized wood surfaces. J. Appl. Polym. Sci. 29, 2777-2784.

Kiguchi, M.1990. Chemical modification of wood surfaces by etherification I. Manufacture of surface hot-melted wood by etherification. Mokuzai gakkaishi 36, 651-658.

Mjoberg, P. J. 1981. Chemical surface analysis of wood fibers by means of ESCA. Cellulose Chem. Technol. 15, 481-486.

Narayanamurti, D. and Singh, J. 1960. Caoutchouc in teak. Composite Wood 7(4), 39-41.

Nussbaum, R. M. 1993. Oxidative activation of wood surfaces by flame treatment. Wood Sci. Technol. 27, 183-193.

Premrasmi, T. and Dietrichs, H. H. 1967. Nature and distribution of extractives in teak (*Tectona grandis* Linn.) from Thailand. The Natural History Bulletin of the SIAM Society 22, 1-14.

Reyes, L. J. 1938. "Philippine woods". Bureau of Printing, Manila, p.479-482.

Rowell, R. M. 1984. "The chemistry of solid wood". American Chemical Society, Washington, D.C.

Ruddick, J. N. R. , Yamamoto, K., Wong, P. C., and Mitchell, K. A. R. 1993. X-ray photoelectron spectroscopic analysis of CCA-treated wood. Holzforschung 47, 458-464.

Sandermann, W. and Dietrichs, H. H. 1959. Chemical studies on tropical woods. IV. Chemical researches on teakwood. Holzforschung 13, 137-148.

Sandermann, W., Dietrichs, H. H., Simatupang, M. H., and Puth, M. 1963. Untersuchungen uber kautschukhaltige Holzer. Holzforschung 17, 161-168.

Sandermann, W. and Simatupang, M. H. 1966. On the chemistry and biochemistry of teakwood (*Tectona grandis* L. fil). Holz als Roh- und Werkstoff. 24, 190-204.

Ser, C. S. and Neo, S. L. 1982. The susceptibility of some Malaysian timbers to iron stains. Malaysian Forester 45, 425-430.

Simatupang, M. H. and Rosamah, E. 1994. Unpublished results.

Timell, T. E. 1958. Pulp Pap. Mag. Can. 59(8), 139-140.

Yamamoto, K. and Inoue, M. 1990. Difference of CCA efficacy among coniferous wood species. International Research Group on Wood Preservation. Document No: IRG/WP/3601, pp.10.

Yamamoto, K. and Ruddick, J. N. R. 1994. Application of x-ray photoelectron spectroscopy to CCA-treated wood. Wood Protection 2, 75-82.